



Adsorptive and Photocatalytic Removal of Rhodamine B Dye from Water by using Copper Ferrite Polyaniline Nanocomposite

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Preparation of copper ferrite polyaniline nanocomposite (CF-PANI) and its use for photocatalytic degradation of Rhodamine B dye from aqueous solution has been studied. Copper ferrite (CuFe_2O_4), a magnetic ferrite (spinel) of nano dimension was synthesized by co-precipitation method. Polyaniline nanocomposite of copper ferrite was prepared by in situ polymerization and SEM technique was used for characterization. Adsorption and photo-degradation capacity of prepared nanocomposite was evaluated under different conditions.

Keywords: CF-PANI nanocomposite, Sunlight, Degradation, Kinetics

Introduction

More than 10,000 chemically different dyes are being used in textile manufacturing.^{1,2} Dyes are harmful to living being as they show toxic, carcinogenic, and mutagenic effect on environment.^{3,4} Out of all, Rhodamine B (RhB) dye is widely used for dyeing silk, wool, and nylon. For the removal of dyes from aqueous solution, adsorption cum photo-catalytic degradation is found to be very effective.⁵ Spinel ferrites possess unique properties of adsorption due to porous structure. Because of optimum band gap energy to absorb visible light, spinels act as photo-catalysts for degradation of dyes.^{6,7} In the present paper Copper ferrite-polyaniline nanocomposite (CF-PANI) has been used for removal and photo degradation of RhB dye from aqueous solution under different conditions. Results have been discussed.

Material and Methods

Materials

Chemicals with high purity approximately 99% were used for the study. Copper Sulphate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] (Qualigens), Ferric Nitrate [$\text{Fe}(\text{NO}_3)_3$] (Fisher Scientific), Aniline [$\text{C}_6\text{H}_5\text{NH}_2$] (Merck), Toluene [$\text{C}_6\text{H}_5\text{CH}_3$] (Merck), Ammonia and Rhodamine B dye were used without further purification.

Methodology

Preparation of Copper ferrite (CuFe_2O_4)(CF)

One molar copper sulphate and 2 molar ferric nitrate were mixed well in distilled water. Ammonium hydroxide (NH_4OH) solution was then added for precipitation. Precipitate obtained was washed with hot water and dried at 100°C , and then heated in a furnace at 500°C for 3 h. Copper ferrite nanoparticles were formed.

Preparation of polyaniline (PANI)

Aniline and toluene were mixed in 1:4 molar ratio. Copper sulphate (CuSO_4) solution of 0.1M concentration was added for polymerization. The product was left for 6–8 h, where a precipitate was obtained. To get polyaniline (PANI) it was washed and heated for 10 h at 100°C .

Synthesis of CuFe_2O_4 -PANI nanocomposite (CF-PANI)

During the polymerization process of polyaniline, CuFe_2O_4 (10% of PANI, 0.32 g) was added and mixed well using magnetic stirrer. A precipitate obtained was filtered and washed with hot water, dried at 80°C for 2 h. The CuFe_2O_4 -PANI nanocomposite was formed.

Preparation of solution of Rhodamine B dye

Rhodamine B (RhB) ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) is a xanthenes dye and cationic in nature. Stock solution of RhB was prepared at 20 mg/L strength with distilled water. Further dilutions of 5 mg/L, 10 mg/L and 15 mg/L solutions were prepared from the stock solution.

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Spectroscopic study

There was an addition of 0.2g CuFe₂O₄-PANI into 20mg/LRhB dye solution and kept in dark and Sun light. Concentration of RhB dye before and after adsorption by CuFe₂O₄-PANI was determined using UV-Visible spectrophotometer at λ_{\max} 553nm at different intervals of time (5–50 min).

SEM study

Scanning electron microscopy (SEM) was used to study the surface morphology of adsorbents.

Results and Discussion

Surface morphology

Surface morphology of copper ferrite (CF) and copper ferrite polyaniline (CF-PANI) nanocomposite was recorded by using SEM. SEM images of copper ferrite and CF-PANI nanocomposite are shown in Fig. 1 (A & B). Copper ferrite has nano dimension and the particles appear to be agglomerated (Fig. 1A).

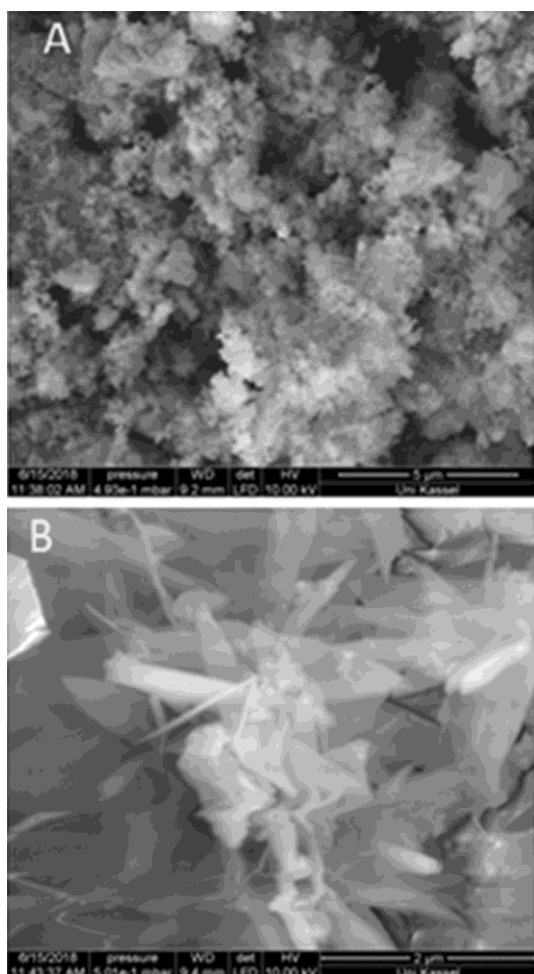


Fig. 1 — (A) SEM image of Copper Ferrite and (B) CF-PANI nanocomposite

However, Fig.1B shows that CF-PANI nanocomposite has fibrous and crystalline morphology and the agglomeration is decreased considerably.

Rhodamine B dye removal from aqueous solution

Effect of contact time

The removal of RhB dye in presence and absence of sunlight was estimated up to 50 minutes and the maximum removal of 95% was found in presence of sunlight and 72% in absence of sunlight within 45 minutes and after that there was no removal of dye. This may be attributed to decrease in available sites after attaining equilibrium.

Effect of concentration of Rhodamine B dye

Removal of RhB dye from aqueous solution was carried out in the concentration range of 5–20 mg/L with 0.2 g dose of CF-PANI nanocomposite. It was observed that percentage removal of dye was much higher in the presence of sunlight as compared to that in dark. Removal decreased with concentration of dye. In presence of sunlight colour change occurred and after 45 minutes in presence of adsorbent, almost entire colour vanished (Fig. 2).

Effect of pH

Effect of pH (2–10) on removal of dye was examined and found that as the pH increased, percentage removal of dye increased and reached to 90% in presence of sunlight. The influence of pH was more at pH > 6.0 which could be explained on the basis of pH_{zpc} of CF-PANI nanocomposite

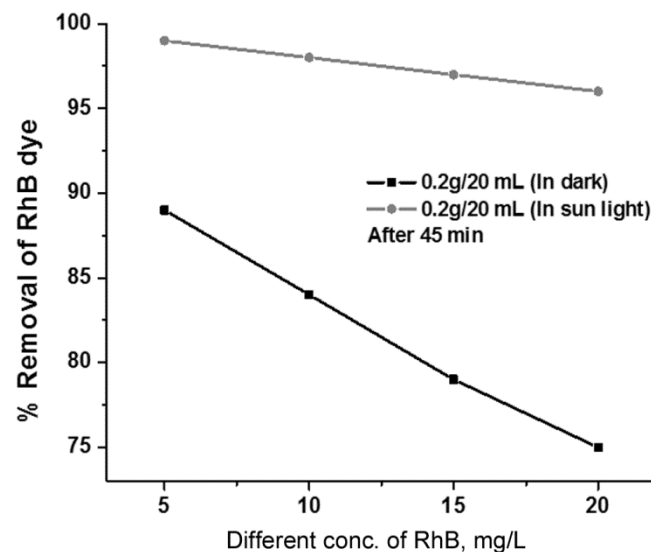


Fig. 2 — Effect of RhB dye concentration on its removal by CF-PANI nanocomposite (0.2 g/20 ml) in sunlight and dark

adsorbent. The pH_{zpc} of CF-PANI nanocomposite was evaluated at pH 6.0, indicating that nanocomposite surface was highly protonated at pH below 6, while surface became negatively charged at pH above 6.

Adsorption Isotherms

Different adsorption models were tested to fit the data (Table 1) and graphs plotted (Fig. 3). On the basis of R^2 values, given in Table 1, it was found that Langmuir model fitted the data best.

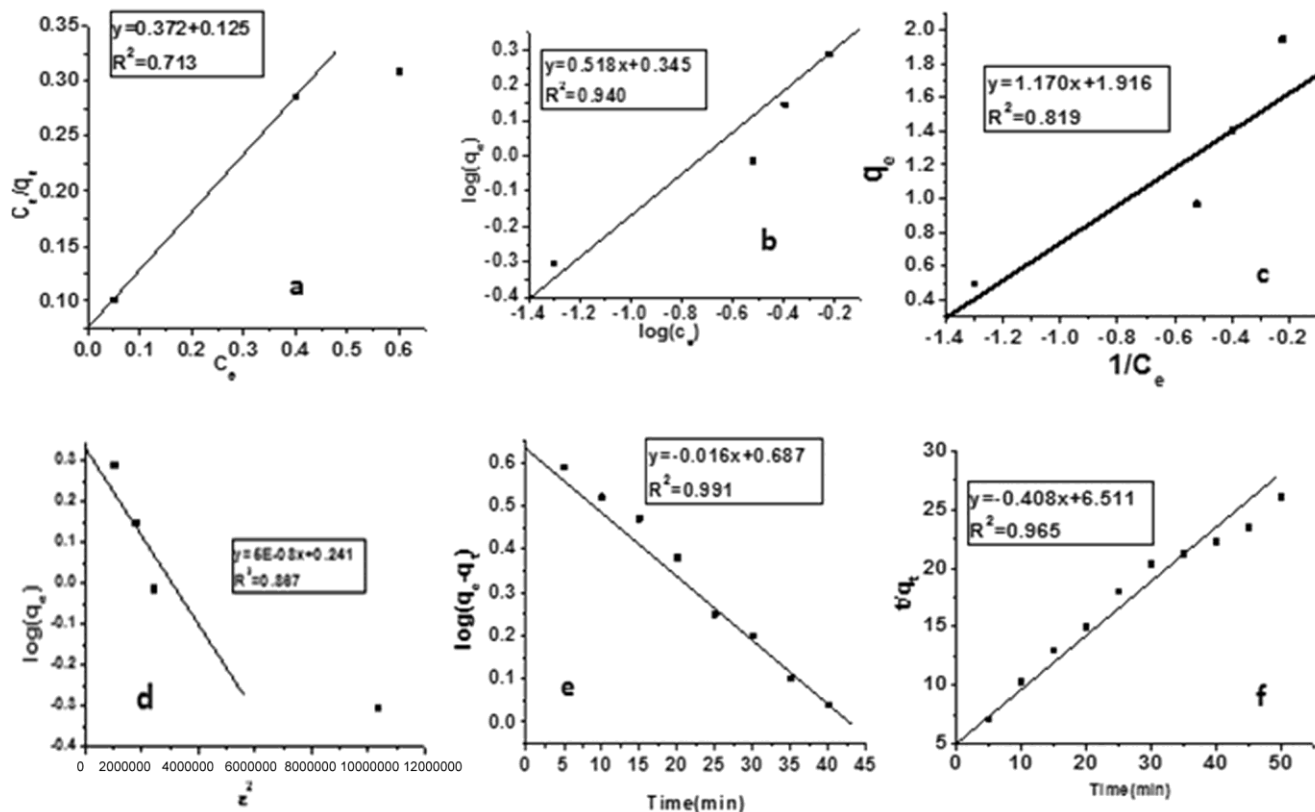


Fig. 3 — Verification of (a) Langmuir isotherm (b) Freundlich isotherm (c) Temkin isotherm (d) D-R isotherm (e) pseudo first order and (f) Pseudo second order kinetic models

Table 1 — Adsorption isotherm and Kinetics parameters for various models

Adsorption isotherms	Equations	R^2	Parameters
Langmuir adsorption isotherm	$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m}$	0.95	$b=0.13$ $q_m=13.69$
Freundlich isotherm	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	0.94	$K_f=2754$ $n=6.329$
Temkin isotherm model	$q_e = B \log A + B \log c_e$	0.819	$A=10$ $B=1.17$
D-R isotherm model	$\ln q_e = \ln Q_0 - K_{DR} \varepsilon^2$	0.867	$X_m=257$ $\beta=2.19$
Adsorption kinetics	Equations	R^2	Parameters
Pseudo-first-order kinetic model	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	0.921	$q_e(\text{mg/g})=15.8,$ $C_0(\text{mg/L})=20$ $k_1(\text{1/min})=0.437$
Pseudo-second-order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	0.996	$q_e(\text{mg/g})=2.45$ $k_2(\text{g/mg/min})=0.038$

Adsorption Kinetics

The adsorption data fitted pseudo second order kinetic model best (Table 1).

Regeneration capacity

CF-PANI nanocomposite can be regenerated after Rhodamine B dye removal and after four times regeneration it removed 70% of dye.

Conclusions

The prepared copper ferrite polyaniline nanocomposite showed excellent adsorption and photo-catalytic degradation capacity for Rhodamine B dye from aqueous solution. It removed 90% of Rhodamine B dye within 45 minutes in the pH range of 6 to 8, in presence of sunlight. The adsorption process followed pseudo second order kinetics and Langmuir adsorption isotherm model.

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